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Kurzmitteilung

Polymerization of Cyclobutene and of 3-Methylcyclobutene by $RuCl_3$ in Polar Protic Solvents

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In previous papers [1,2] we reported that cyclobutene can be polymerized by ZIEGLER catalysts to polymers with either polycyclobutene or polybutadiene structure. The formation of the two different types of polymers mainly depends on the particular transition metal contained in the catalyst. Thus, catalysts prepared from Ti compounds and aluminum alkyls yield polymers having prevailingly polybutadiene structure, whereas those prepared from V or Cr compounds and aluminum alkyls generally yield crystalline polymers having pure polycyclobutene structure.

More recently we succeeded in polymerizing cyclobutene to crystalline polycyclobutene using aqueous solutions of $RhCl_3$ [3] or alcoholic solutions of π-allyl-Ni-bromide [4] as catalysts.

These findings suggested to us the hypothesis [3,4] that such 8th group metal salts in protic solvents (*e.g.*, H_2O or alcohol) recently proposed for the stereospecific polymerization of butadiene [5,6], act, analogously to the ZIEGLER catalysts, through an anionic coordinated mechanism. By this definition we mean that the growth of the polymer chain occurs by insertion of the monomer at a polarized metal-carbon bond, preceded by a coordination of the monomer to the transition metal.

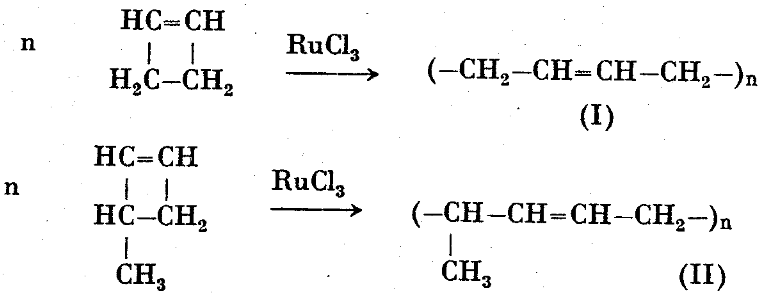
For further confirmation of this hypothesis, we thought it useful to extend our investigations on cyclobutene polymerization in polar protic solvents to the $RuCl_3$ catalyst system [6]. In order to provide a larger basis to our research, we have also included polymerization studies on 3-methylcyclobutene. The polymerization of this monomer does not seem to have been studied as get.

Table 1. Polymerization of cyclobutene and 3-methylcyclobutene in the presence of $RuCl_3$-protic solvent systems
(under nitrogen; polymerization time 100–150 hrs.; monomer/$RuCl_3$ molar ratio = 100)

Monomer	Medium	Temp. (°C.)	Polym. yield (%)	Butadiene units in the polymer[c] (%)		Properties
				1,4-*cis*	1,4-*trans*	
Cyclobutene	water[a]	50	10	50	50	benzene soluble oil
Cyclobutene	ethanol[b]	20	15	0	100	benzene soluble crystalline powder $\overline{M}_n = 2.900$[d] m.p. ≈ 90 °C.[e]
3-Methyl-cyclobutene	water[a]	50	15	65	35	benzene soluble oil
3-Methyl-cyclobutene	ethanol[b]	20	20	15	85	benzene soluble wax

[a] 1 vol. monomer + 2 vol. water containing 1% Na-dodecyl benzene sulfonate;
[b] 1 vol. monomer + 6 vol. ethanol; [c] by IR method;
[d] Mechrolab vapor pressure osmometer; [e] by polarizing microscope.

Cyclobutene as well as 3-methylcyclobutene are polymerized in the presence of $RuCl_3$ – protic solvent systems exclusively *via* ring cleavage (Table 1). The polymers of cyclobutene and of 3-methylcyclobutene thus obtained are consequently built up only by butadiene 1,4 (I) and pentadiene 1,4 (II) units respectively:



$$n\ \text{cyclobutene} \xrightarrow{RuCl_3} (-CH_2-CH=CH-CH_2-)_n \quad \text{(I)}$$

$$n\ \text{3-methylcyclobutene} \xrightarrow{RuCl_3} (-CH(CH_3)-CH=CH-CH_2-)_n \quad \text{(II)}$$

Isoprene units are completely absent in the polymers obtained from 3-methylcyclobutene (absence of the absorption band at 11.9 μ in the IR spectrum, due to trisubstituted double bonds). This means that the polymerization of 3-methylcyclobutene *via* ring cleavage does not involve shift of the double bond towards the methyl group.

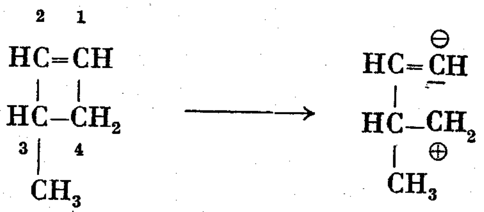
Interesting considerations can be deduced from the examination of the end groups of the obtained polymers. Polybutadienes obtained either in water or in alcohol show characteristic absorptions in the IR spectrum, the intensity of which in relation to the molecular weight of the polymers allows us to consider them to be end groups:

1) A couple of bands, at 5.06 and 5.16 μ, in the polymers obtained in alcohol and a single band at 5.20 μ in the polymers obtained in H_2O. These three bands can be attributed to allene groups.
2) A band at 11.0 μ characteristic of vinyl groups.
3) A band at 7.30 μ characteristic of methyl groups.

Also, the IR spectrum of polypentadiene shows characteristic absorption bands, most likely derived from end groups:

1) A couple of bands at 5.06 μ and 5.16 μ, attributable to end groups of the allene type.
2) A band at 11.30 μ, characteristic of the vinylidene groups.

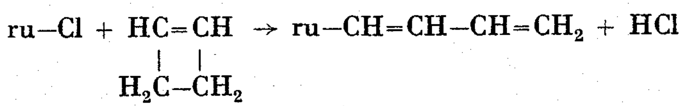
These data permit some indications on the type of opening of the cyclobutene ring. The fact that polymers having polybutadiene structure show vinyl end groups, while those having pendadiene structure show vinylidene end groups in equivalent amounts means that the latter derive from the methyl substituent contained in 3-methylcyclobutene. It can be undoubtedly deduced from this premise that the ring cleavage of 3-methyl-cyclobutene, which yields a pentadiene unit, occurs between the carbon atoms 1 and 4 of the ring



If the ring cleavage would occur in the 2–3 or 3–4 position no possibility for formation of vinylidene end groups could be foreseen.

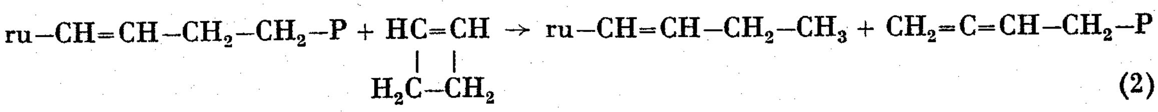
This deduction of the site of opening of the ring fully agrees with our previous assumption1) for the polymerization of cyclobutene to polybutadiene and of cyclopentene to polypentenamers7). From considerations on the isomerization of the double bond, and from what was already known on the polymerization of norbornene, we had in fact assumed that the cycloalkene rings should open at the single bond adjacent to the double bond.

An initiation and termination mechanism of the chains which unequivocally accounts for all the end groups reported above is not easy to be formulated at this moment. We therefore limit us to propose a scheme which might explain the mere presence of vinyl, vinylidene, allene and methyl end groups in the polymers. The vinyl groups in the polybutadienes (or vinylidene groups in polypentadienes) should derive, according to this mechanism, from a chain initiation, involving the formation of a Ru-C bond with evolution of HCl; the overall reaction of this initiation should correspond to the transfer of a proton from the monomer to $RuCl_3$. According to this assumption we find free hydrochloric acid in the polymerization medium (ethanol). Reactions of this type between an olefin and Pd or Rh chlorides are well known in organometallic chemistry[8,9].



$$\mathrm{ru{-}Cl} + \begin{array}{c}\mathrm{HC{=}CH}\\ |\quad\; |\\ \mathrm{H_2C{-}CH_2}\end{array} \rightarrow \mathrm{ru{-}CH{=}CH{-}CH{=}CH_2} + \mathrm{HCl} \qquad (1)$$

The formation of the allene and the methyl groups might be derived from a transfer between the growing chain and the monomer, involving a hydride ion transfer from the terminating chain to the monomer starting a new chain and simultaneously, a hydrogen shift in the terminated chain.



$$\mathrm{ru{-}CH{=}CH{-}CH_2{-}CH_2{-}P} + \begin{array}{c}\mathrm{HC{=}CH}\\ |\quad\; |\\ \mathrm{H_2C{-}CH_2}\end{array} \rightarrow \mathrm{ru{-}CH{=}CH{-}CH_2{-}CH_3} + \mathrm{CH_2{=}C{=}CH{-}CH_2{-}P} \qquad (2)$$

Independently of the reliability of these schemes which require further experimental evidences we wish to point out that the presence of the end groups mentioned above agrees exclusively with an anionic co-ordinated nature of the polymerization. Consistent with this fact is also the observation that a great part of the Ru is retained by the polymer even after treatment with boiling ethanol-HCl mixture.

The obtainment of polybutadienes and polypentadienes from cyclobutene and methylcyclobutene respectively, in the presence of $RuCl_3$ provides a further analogy between the Ziegler catalysts and the catalysts based on salts of metals of the 8th group, acting in a polar protic medium.

Table 2. Behaviour of different transition metals in the homopolymerization of cyclobutene

Catalyst system		Monomer units contained in the polymer		
		Cyclobutene (%)	Butadiene (%)	
			1,4 *cis*	1,4 *trans*
$RuCl_3$	in water	0	50	50
$RuCl_3$	in ethanol	0	0	100
$RhCl_3$	in water	99	0	1
$RhCl_3$	in ethanol	98	0	2
π-Allyl-Ni-bromide	in ethanol	100	0	0
$TiCl_4 + Al(C_2H_5)_3$	in toluene	5	30	65
$MoCl_5 + Al(C_2H_5)_3$	in toluene	30	30	40
$VCl_4 + Al(C_2H_5)_3$	in *n*-heptane	99	0	1
$CrO_2Cl_2 + Al(C_2H_5)_2Cl$	in toluene	100	0	0

As it can be seen from Table 2 the ZIEGLER catalysts containing Ti polymerize cyclobutene to polybutadiene, while those based on V or Cr yield polymers having polycyclobutene structure. Among the catalysts acting in a protic solvent medium we find that Ru yields polymers with polybutadiene structure while Rh and Ni yield polymers with polycyclobutene structure.

We can, therefore, stress the following two series of transition metals each exhibiting increasing activity in ring cleavage and, consequently, decreasing activity in opening of the double bond in the polymerization of cyclobutene monomers:

Cr–V–Mo–Ti and Ni–Rh–Ru

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